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Formation of stable neutral copper *bis*-dithiolene thin films by potentiostatic electrodeposition**

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^[†]Electronic supplementary information (ESI) available. See <http://dx.doi.org/10.1039/C1CC12344K>

Abstract

Functional thin films of neutral copper dithiolenes have been prepared by potentiostatic electrodeposition. This method allows the isolation of near infrared (NIR) active species, in a useable form, that are otherwise unobtainable by conventional chemical methods.

Introduction

The preparation of thin films of NIR active materials is an active area of research within materials chemistry, with potential applications such as organic photodetectors,¹ electrochromic devices² and broad spectrum photovoltaics.³ Neutral and anionic metal *bis*-dithiolenes of Ni, Pd, Pt⁴ and neutral analogues of Au⁵ characteristically show strong absorption in this region and, coupled with numerous reports of semiconductive behaviour,⁶ are therefore interesting targets for optoelectronic application. Isoelectronic with the neutral Au and monoanionic Ni, Pd, Pt dithiolenes, neutral Cu dithiolenes are expected to show very low energy NIR absorption due to an intense $\pi \rightarrow \pi^*$ transition predominantly within the ligand moieties,⁷ however, study into such systems has been limited due to their poor stability in solution, prohibiting their isolation.[‡]

We here report the fabrication of thin films of two novel neutral copper dithiolenes, [Cu(mi-5edt)₂] (**1**) and [Cu(mi-5hdt)₂] (**2**) (Fig. 1), by potentiostatic electrodeposition from their isolable monoanionic TMA salts and, by investigation of their optical and redox properties, demonstrate that such species are only obtainable by this direct fabrication method⁸ [(mi-5edt) = 1-(*N*-methylindol-5-yl)-ethylene-1,2-dithiolate; (mi-5hdt) = 1-(*N*-methylindol-5-yl)-hex-1-ene-1,2-dithiolate; TMA = tetramethyl-ammonium].

We have previously reported the synthesis of a stable ligand precursor for (mi-5hdt).² The route to the analogous (mi-5edt), as well as details of the synthesis of both monoanionic copper salts, is given in the ESI[†]. Deprotection of the ligand precursors was first attempted using NaOMe/MeOH, and subsequent addition of CuCl₂·2H₂O. For mi-5edt, this method resulted in the immediate precipitation of, what was suggested by elemental analysis to be neutral **1**, and not the monoanion, contrary to other structurally analogous systems.⁹ However, the complex was shown to be unstable in the few solvents in which it was soluble (DMF and DMSO), and thus a rigorous molecular characterization was prohibited. Formation of the stable monoanionic salt of **1** could be achieved using [TMA][OH] as a base in THF, followed by addition of CuCl₂·2H₂O, and leaving the flask open to atmospheric oxidation, with pure [TMA][**1**] precipitating slowly from solution upon cooling, and which could be isolated as a dark brown precipitate by filtration (42 %).

For mi-5hdt, reaction of the ligand precursor with NaOMe/MeOH, followed by dropwise addition of CuCl₂·2H₂O did not lead to the immediate precipitation of the neutral dithiolene, as for **1**, but instead the complex remained in solution until it was added to a methanolic solution of PPh₄Br, whereupon the complex precipitated as the monoanionic tetraphenyl-phosphonium salt [PPh₄][**2**], in rather poor yield (15 %).

Improved yields of a monoanionic salt could be achieved using the [TMA][OH]/THF route, as for **1**, with pure [TMA][**2**] isolated by filtration as a bronze precipitate (46 %).

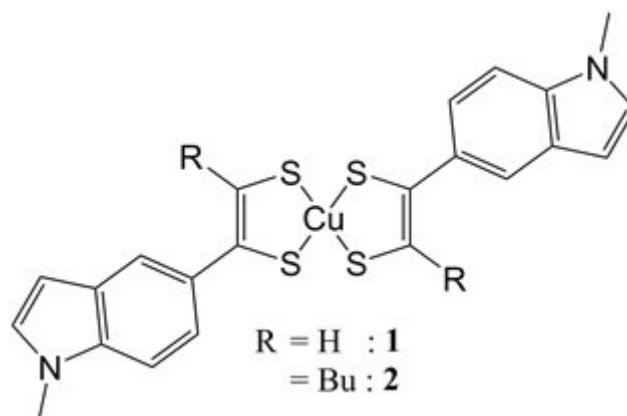


Figure 1. Structures of the copper bis-dithiolenes used in this study: $R=H:Cu(mi-5edt)_2$ (**1**), and $R=Bu:Cu(mi-5hdt)_2$ (**2**).

The TMA salts of **1** and **2** showed only very weak absorption in the NIR region at 1557 nm (6423 cm^{-1} , $\epsilon = 550$) and 1486 nm (6729 cm^{-1} , $\epsilon = 523$) for [TMA][**1**] and [TMA][**2**], respectively (Fig. S1, ESI[†]). By comparison with the redox series of the nickel dithiolenes, the monoanionic copper dithiolenes are isoelectronic with the dianionic nickel dithiolenes.⁷ The comparative weakness of the NIR absorptions, compared to their monoanionic nickel analogues,² can thus be understood, since the orbital corresponding to the SOMO in the monoanionic nickel dithiolenes, is filled for the monoanionic copper systems, and thus prohibits an analogous $\pi \rightarrow \pi^*$ transition.⁷ The weak NIR absorption observed for [TMA][**1**] and [TMA][**2**], is therefore likely due to $d \rightarrow d$ transitions on the copper centre.

Both complexes showed one strong absorption in the UV/Vis region of the electromagnetic spectrum [418 nm ($23,923\text{ cm}^{-1}$, $\epsilon = 11,220$) for [TMA][**1**] and 393 nm ($25,445\text{ cm}^{-1}$, $\epsilon = 26,181$) for [TMA][**2**]], and a second absorption outside the solvent window for spectroscopic investigation. The intensity and energy of the UV/Vis transition suggests it to be a ligand centred transition. Over several days, the spectra of [TMA][**1**] changed, losing the peak at 418 nm, with the resulting spectrum reminiscent of that of chemically synthesised **1** upon dissolution/decomposition in DMF. This suggests that [TMA][**1**] is slowly oxidised in solution, whereupon it undergoes the same fate as observed for chemically synthesised neutral **1** in solution. This might explain the difficulties encountered for single crystal growth of [TMA][**1**], and isolation of the monoanionic complex from the NaOMe/MeOH route. Such a process is not observed for [TMA][**2**], suggesting that it is more resistant to oxidation, possibly due to a more out-of-plane indolyl group (due to greater steric hindrance from the -Bu group), not raising the HOMO level as much as for [TMA][**1**].⁸

The electrochemistry of both [TMA][1] and [TMA][2] was investigated in a 0.1 M TBABF₄ electrolyte solution of MeCN (Fig. S2, ESI[†]). Both complexes showed one electrochemically reversible redox process at $E_{1/2}^1 = -0.59$ V and -0.80 V for [TMA][1] and [TMA][2], respectively. This reversible process, assigned to the [ML₂]^{2-/1-} redox couple, was observed to be highly sensitive to the ligand environment, with the reduction to the dianion occurring at less negative potentials for [TMA][1] than for [TMA][2]. This is likely due to the more in-plane twist of the indolyl group in [TMA][1] being better able to stabilise the development of a second negative charge, through greater delocalisation onto the ligand, than for [TMA][2].

For [TMA][1], a second reduction process was observed ($E_{1/2}^1 = -1.62$), that was shown to be chemically reversible, though not electrochemically reversible, as the associated oxidation current (I_p^{ox}) decreased at faster scan rates. This presumably corresponds to a Cu^{2+/1+} transition, since the ligand environment is already fully reduced. This process is usually associated with a geometry change from (*pseudo*) square-planar to tetrahedral, and thus is not expected to be electrochemically reversible.¹⁰ The fact that an associated oxidation process is observed, at low over-potential, might suggest that the observed geometry change is slight, and that the solution geometry of the monoanion may not be rigorously square planar.¹¹ On cooling the electrochemical cell to -40°C , the reduction process shifted outside the solvent window and, as such, no associated oxidation process was observed. On scanning to positive potentials, an irreversible process was observed at $E_{ox}^3 = 0.42$ V and 0.45 V for [TMA][1] and [TMA][2], respectively, corresponding to a [ML₂]^{1-/0} transition, followed by several other irreversible oxidation processes. In MeCN, this first oxidation process led to the deposition of a film on the electrode surface for both [TMA][1] and [TMA][2]. For both complexes, by scanning the coated electrode back to negative potentials, past E^2 , a greater reduction current (I_p^{red}) was observed, at the same potential as for E^2 , compared to an identical scan cycle for a clean electrode (Fig. 2).

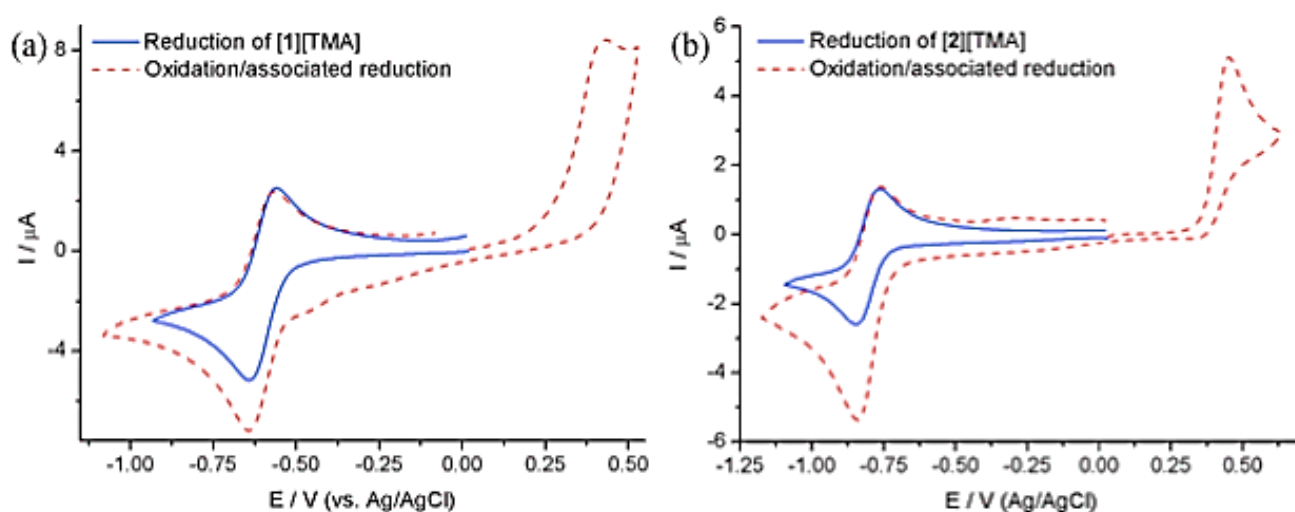


Figure 2. Studies on deposited films of **1** and **2**: (a) associated reduction of the first oxidation process of [TMA][1]; (b) associated reduction of the first oxidation process of [TMA][2]. Both plots show that the films

deposited could be quantitatively reduced at the same potential as for their TMA salts, indicating that intact neutral **1** and **2** had been deposited on the electrodes. Axes depict current (I) in response to an applied voltage (E).

On scanning back to positive potentials, past E^2 , no increase in the oxidation current (I_p^{ox}) was observed compared to the clean electrode. This suggested that the deposited films were comprised of the neutral species (**1** or **2**), and were molecular in nature, due to their identical redox behaviour to the monomer in solution. The formed neutral films could then be quantitatively reduced, and thus redissolved, by scanning past E^2 .

When a similar experiment was performed in an identical electrolyte solution of DMF, an irreversible oxidation process was observed for E^3 , however, no film was observed to form on the electrode and, upon scanning back past $E_{1/2}^2$, no increase in peak current was observed for the reduction or oxidation process. This different behaviour is consistent with the electrogeneration of a species that is unstable when solubilised in the DMF solvent system.

In order to further characterise the electrogenerated films of **1** and **2** from MeCN, films were grown on fluorine doped tin oxide (FTO) coated glass electrodes, so that the electronic absorption properties could be investigated. Continuous amorphous films of **1** and **2** (observed by SEM and thin film XRD, Fig. S5, ESI[†]) were grown under potentiostatic control, by maintaining a constant potential ($E = 0.5$ V and 0.6 V for the electrodeposition of **1** and **2**, respectively), and recording the charge passed with time (Fig. S3, ESI[†]). The deposited film of **1** was shown to be more conductive than **2**, due to the passing of a greater current at the working electrode, however both **1** and **2** continued to grow on the working electrode, resulting in the formation of continuous films, that were gold in colour, for both complexes. The UV/Vis/NIR absorption spectra of both complexes showed pronounced differences from their respective monoanions, investigated in solution (Fig. 3a). Both complexes showed an intense absorption in the NIR range [~ 1270 nm ($7,849$ cm⁻¹ for both **1** and **2**)], as well as several other absorptions across the visible region of the spectra. This suggested that the formed films were indeed neutral molecular copper *bis*-dithiolenes, with the oxidation processes corresponding to the loss of an electron from the dithiolene ligand, thus facilitating an intense $\pi \rightarrow \pi^*$ transition, as observed for the isoelectronic monoanionic nickel dithiolenes.

The films of neutral **1** and **2**, deposited from MeCN, were completely soluble in DMF, however, the UV/Vis spectra of the dissolved films were shown to be very different from those in the solid-state, losing all the absorption processes in the visible and NIR regions of the spectra (Fig. 3a), resembling the spectra for **1** in DMF, formed by chemical synthesis, which was shown to decompose upon dissolution. It is therefore apparent that electrodeposition provides a route to thin films of neutral **1** and **2** that are otherwise unobtainable by solution methods.

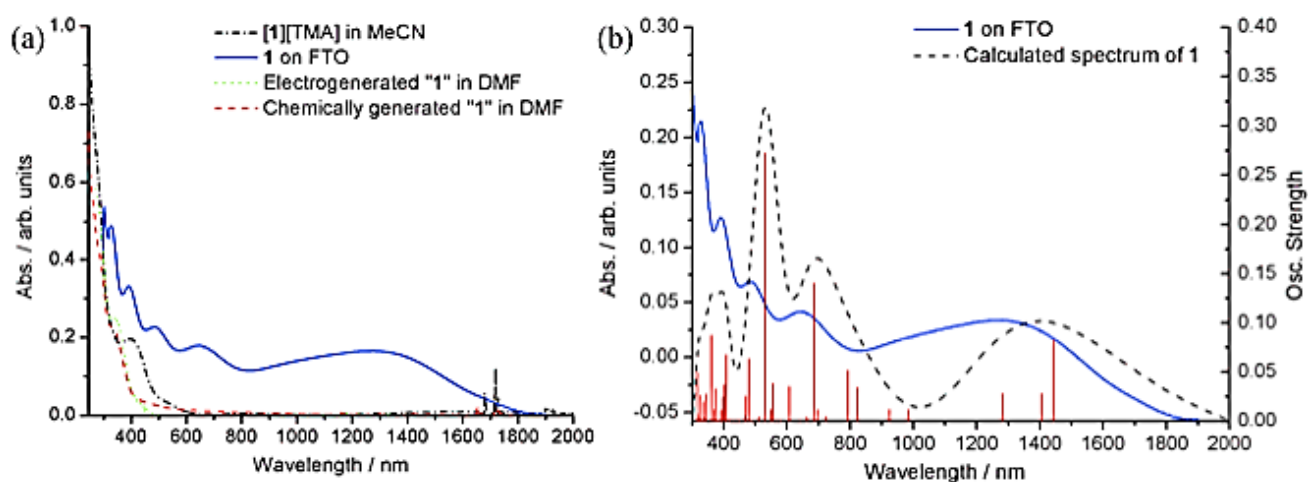


Figure 3. Experimental and calculated UV/Vis/NIR spectroscopy of an electrodeposited film of neutral **1** on FTO; (a) Thin film spectra, compared to the stable monoanionic complex [TMA][**1**] in MeCN, and showing the decomposition of neutral **1** upon dissolution. Quotation marks “x” denote that the species is no longer its identity upon dissolution, due to an unknown decomposition process; (b) Thin film spectrum of **1** compared to calculated spectra from TD-DFT.

In order to shed more light on the nature of the absorption of the deposited complex, density functional theory (DFT) calculations were performed on a modelled complex of **1**, using the same level of theory as has proven successful for an analogous nickel complex² ((U)B3PW91/6-31G*).¹²⁻¹⁵ Removing symmetry constraints, and starting from an idealised tetrahedral geometry,^{16,17} geometry optimisation showed the complex to converge upon an energy minimum that can be best described as a squashed tetrahedron, with the two dithiolene rings distorted by 43.56° away from co-planarity. Following geometry optimisation, information regarding the nature of the electronic transitions for **1** was sought using time-dependent density functional theory (TD-DFT). This was done to model the electronic absorption spectrum, for comparison with the electrodeposited thin films, and to probe the origins of the individual absorptions. TD-DFT calculations showed reasonable agreement with the experimentally determined absorption spectrum (Fig. 3b), and showed the low energy NIR absorption to be predominantly due to a HOMO→LUMO transition (Table S2, ESI[†]). Since these orbitals are almost exclusively located on the dithiolene SCCS cores (Fig. S4, ESI[†]), this may explain the relatively small difference in energy of the NIR absorption in the absorption spectra of both films ($\Delta\lambda_{\text{NIR}} \approx 31 \text{ nm}$). The thin film spectrum was generally well reproduced by TD-DFT, consistent with a film formed of neutral copper dithiolene complexes, and that the low energy NIR absorption was due to a $\pi \rightarrow \pi^*$ transition within the ligand moieties – analogous to the isoelectronic monoanionic nickel dithiolenes.⁷ It should be noted that copper dithiolenes have been shown to have hugely variable coordination geometry around the metal centre, and that the solution geometry (and thus the colour) is not always the same as that in the solid state.¹⁸ Within this limitation, the consistency between the calculated and experimental spectra is striking.

In summary, by exploiting the reduced solubility of the neutral species, compared to the monoanionic species, thin films of two neutral copper dithiolenes, highly active in the NIR region, were prepared. We have previously reported on the use of electrodeposition as a novel route to fabricate thin films of nickel *bis*-dithiolenes, whose solubility is too low, and melting point too high for effective processing by solution, or vapour methods, respectively.⁸ This study demonstrates an additional benefit of film formation by electrodeposition, where a functional, robust thin film can be prepared, even for a class of compounds where the solution stability has previously proven prohibitively low to allow conventional isolation.

Notes and references

[*]The chemical¹⁶ and electrochemical¹⁷ preparation of a neutral copper dithiolene has previously been reported. However, it is likely that it is the TTF-functionalised ligands, used in both these systems, that are oxidised, rather than the dithiolene core. It is noteworthy that neither study analysed the solution properties of these species, likely due to poor solubility.

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